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Influence of Phosphorous in Magnetic and Corrosion Properties of Electrodeposited Cobalt based Multinary Alloys

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Abstract: In recent past magnetic alloys grabs more attention among the researchers because of their interesting magnetic behavior and potential applications. Cobalt based alloys were immensely studied with several alloy combinations, in order to yield an advanced magnetic properties for the applications of sensors. Driven by the existing literatures we study here the influence of phosphorous on magnetic behavior of CoNiWP films. This paper highly focuses the comparative investigation of CoNiWP alloys deposited at different current densities and how the presence of phosphorous influences the physical properties in the deposited films.

The structural and morphological properties were confirmed by using X-ray diffractogram and FE-SEM micrographs. Ferromagnetic behavior of the films was confirmed using Vibrating sample magnetometer. Magnetoresistance of the film was studied with the help of four probe method and found to be having a stable GMR behavior. Corrosion behavior of the sample was studied using weight loss method and found to be having a corrosion resistance depend on magnetic elements (Co and Ni) in the film. CoNiWP films deposited at higher current density shows a considerable variation in both magnetic and corrosive properties.

Keywords: CoNiWP alloys, Electrodeposition, magnetic films, GMR, phosphorous electrodeposition

I. INTRODUCTION

The development in magneto resistive technology plays vital role in future decisive devices. Magneto resistance adopted as the main theme in recent research interest, and magneto resistive materials are highly used in several technologies, such as magnetic memories, the read component in magnetic recording heads, and magnetic sensors.[1-2] Over other magneto resistive materials, alloys and multilayers with GMR effect were adopted for many studies.[3-7] GMR effect is commonly exists in an alloy and multilayer structure, where two magnetic layers are disjointed by a non-magnetic layer or antiferromagnetic materials. GMR effect was first discovered in the late 1980s in certain Fe/Cr multilayer structure, since the discovery of this effect it becomes an important aspect for many technologies. Over the years, in many literatures this effect is reported as the influence of scattering of electrons when it goes through a non-magnetic or antiferromagnetic interface.

Even though GMR effect is observed in multilayered thin films with IEC (interlayer exchange coupling), theoretically any material combination with an interfaces between a ferromagnetic and nonmagnetic layer can exhibit GMR effect. [8] This kind of GMR materials are mostly prepared by molecular beam epitaxy, and sputtering techniques [9,10], which needs complicated vacuum arrangement.

Among these methods electro deposition is reported as an easier and cost effective method to acquire GMR rich films and multilayers.[11,12] Properties of the multilayers and films can be easily influenced by changing the deposition parameters, which can be easily achieved in electro deposition. Based on reported literatures cobalt has been highly alloyed with phosphorus content, which strongly influences the magnetic properties.

When phosphorus supplemented magnetic alloys were deposited with organic additives like urea, thiourea it adlib the magnetic properties.[13,14] Hence the present work is keen to prepare CoNiWP alloy film on copper substrate at different current density using electro deposition method. The influence of phosphorous on the properties of electrodeposited films was discussed by studying their structural, morphological, and magnetic properties.

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II. EXPERIMENTAL TECHNIQUE

CoNiWP deposition was processed using a standard two electrode cell (galvanostatic) technique under a controlled environment. The electroplating electrolyte used for the deposition composed of Tri sodium citrate based sulfate bath including cobalt sulfate, Nickel sulfate, sodium tungstate, sodium hypophosphite and boric acid. Sulphate based electrolytes were adopted, since sulfate baths are known to generate lower stress on the film over other electrolytes; we have previously reported [15], a crack free nanostructure ternary films with high coercively prepared using sulfate bath.[16] Hence the present work is dedicated to develop bright and smooth multinary films with better magnetic properties. Electrolyte was prepared by dissolving the chosen salt in DI (de-ionized) water and pH of this electrolyte was adjusted to 5 by adding diluted Hydrochloric acid or diluted sodium hydroxide solution. Nickel and Copper plate of dimension (2.5 x 5) was used as anode and cathode. CoNiWP alloy films were deposited at the different current density (2.5 to 10 mA/cm^2) at 30 minutes of deposition time. After the deposition process, films were carefully taken out from the bath and the remaining resists were cleaned by washing the substrate in distilled water.

III. RESULT AND DISCUSSIONS

A. Structural Properties

Structural properties of the electrodeposited CoNiWP films were studied using X-ray diffractogram and shown in Fig. 1(a), (b), (c), and (d). X-ray diffractogram exhibits strong and high intense peaks which reveal the good crystallinity in the films TABLE I. The grain size of the films was calculated using scherer formula and found to be in the range of nanometer. Further it reveals that the crystallite size in the deposit is contingent on the current density. When the current density is increased it is noted that the plane (100) has considerable growth and it is consistent in all films with slight shift in peak position. The presence of higher cobalt content with phosphorous and tungsten content causes this plane shift in the film. Table 1 shows the structural properties of the deposited films.

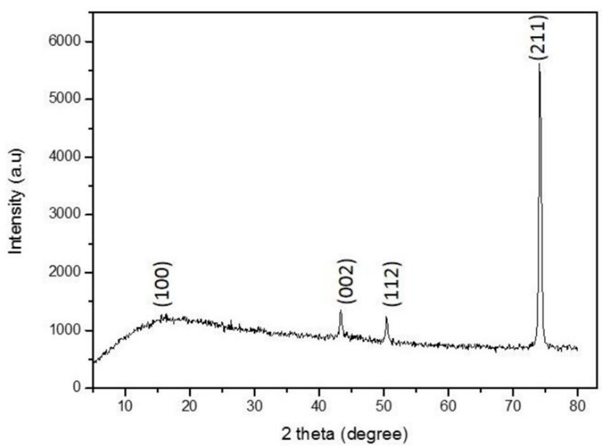

Figure 1 (a) - X-ray diffractogram of CoNiWP films deposited on copper substrate at the current density of 2.5 mA/cm^2

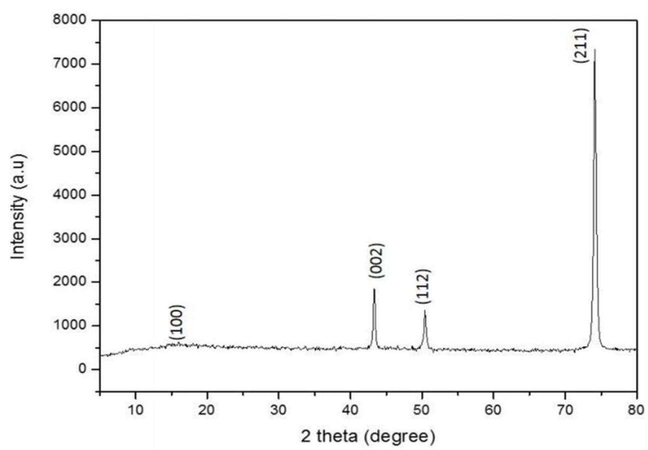

Fig. 1(b) X-ray diffractogram of CoNiWP films deposited on copper substrate at the current density of 5 mA/cm^2

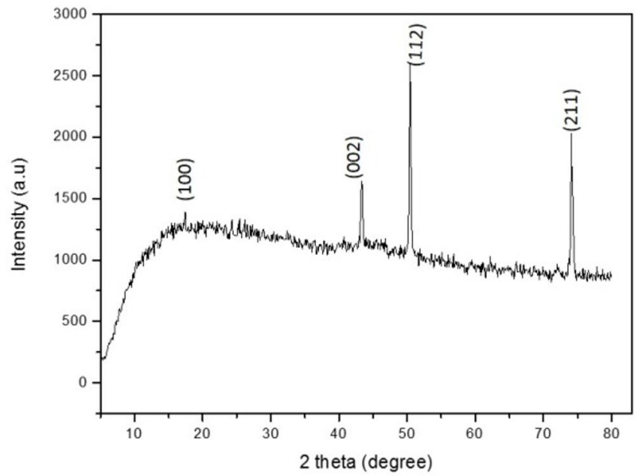

Fig.1(c) X-ray diffractogram of CoNiWP films deposited on copper substrate at the current density of 7.5 mA/cm^2

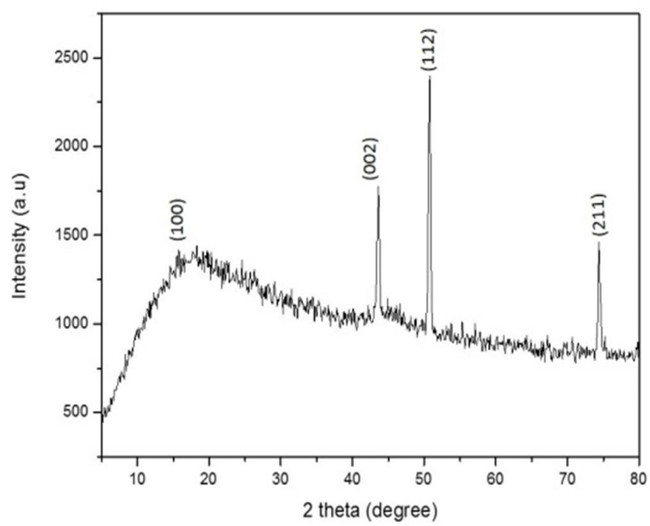

Fig.1(d) X-ray diffractogram of CoNiWP films deposited on copper substrate at the current density of 10 mA/cm^2

Table I Structural Properties Of Coniwp Films At Different Current Density

Bath	Substrate	Concentration (M)	Deposition Time	Current density (mA/cm^2)	Grain size (nm)	Dislocation Density	Lattice strain
Tri sodium citrate bath	Copper	0.1	30 minutes	2.5	18	0.0029	0.0058
				5	22	0.0019	0.0045
				7.5	27	0.0029	0.0037
				10	28	0.0012	0.0040

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B. Confirmation of Constituents in the Films

Fig. 2(a) (b), (c) and (d) shows the EDAX pattern which reveals the presence of constituents in CoNiWP films deposited on copper substrate. The EDAX pattern of the films reveals the presence of relevant peaks such as cobalt, nickel tungsten and phosphorous along with some other impurities. Further it reveals the presence of high level Co, Ni, W, and P content in the films deposited at higher current density. The presence of copper peak is observed which divulges the substrate. [17]

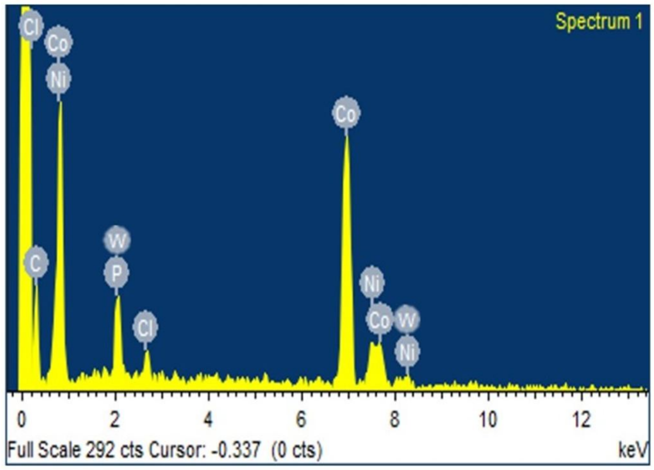

Fig. 2(a) EDAX pattern of CoNiWP films deposited on copper substrate at the current density of 2.5 mA/cm^2

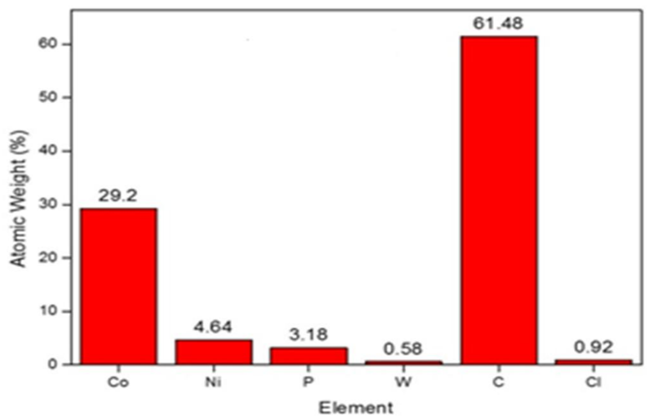

Fig. 2(b) Constituents of CoNiWP films deposited on copper substrate at the current density of 2.5 mA/cm^2

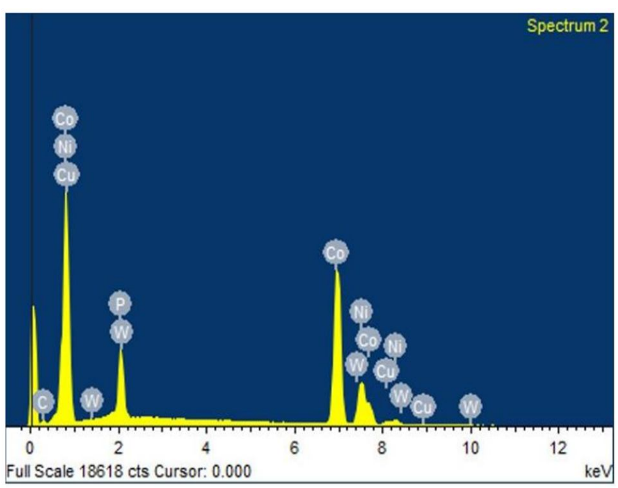

Fig. 2(c) EDAX pattern of CoNiWP films deposited on copper substrate at the current density of 10 mA/cm^2

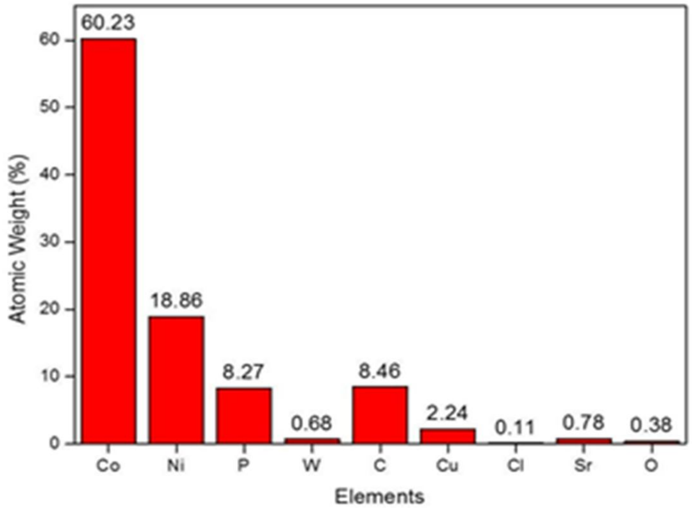

Fig. 2(d) Constituents of CoNiWP films deposited on copper substrate at the current density of 10 mA/cm^2

C. Morphological Properties

Fig. 3(a) (b) (c) and (d) shows the FE-SEM micrographs of electrodeposited CoNiWP films deposited on copper substrate at different current densities. FE-SEM micrographs reveal the uniform formation of films with respect to the current density. The film has uniform, bright and crack free deposits. [18,19] When the current density is increased the deposits are well covered over the substrate. This morphological property is in good agreement with the structural properties.

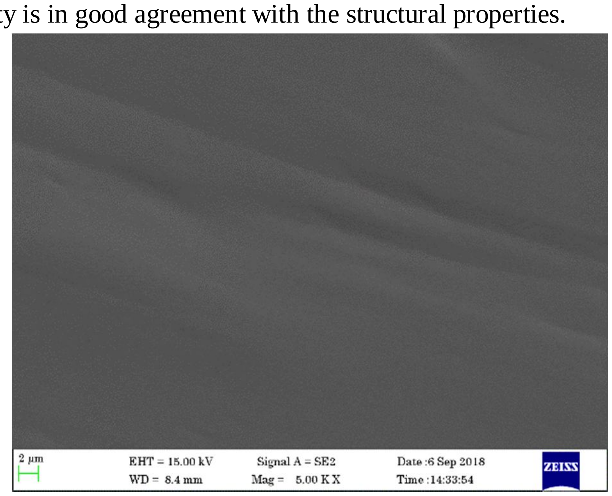

Fig. 3(a) FE-SEM micrograph of CoNiWP films deposited on copper substrate at the current density of 2.5 mA/cm^2

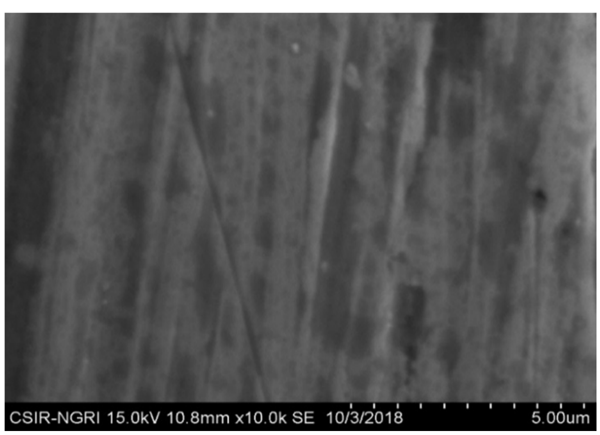

Fig.3 (b) FE-SEM micrographs of CoNiWP films deposited on copper substrate at the current density of 5 mA/cm^2

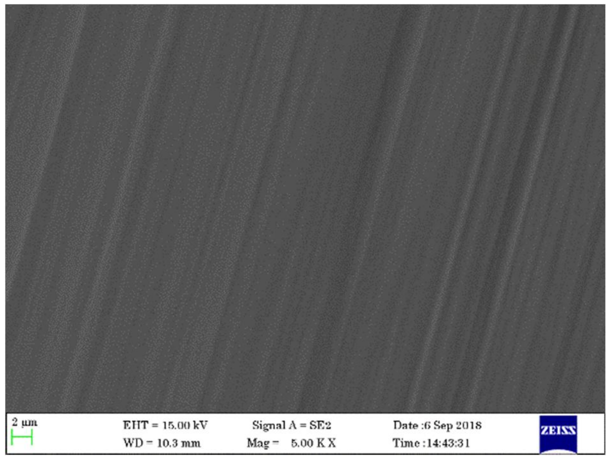

Fig. 3 (c) FE-SEM micrographs of CoNiWP films deposited on copper substrate at the current density of 7.5 mA/cm^2

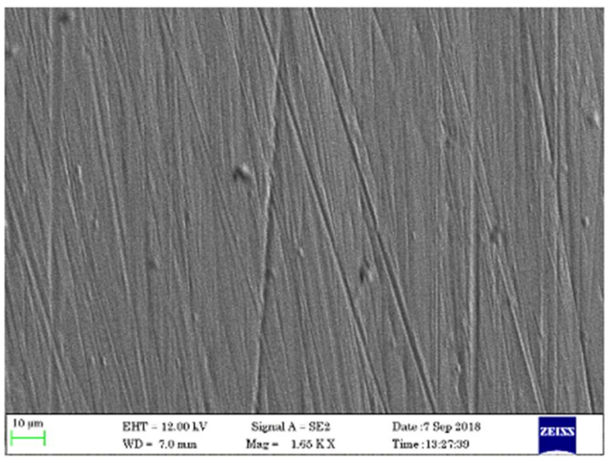

Fig 3 (d) FE-SEM micrograph of CoNiWP films deposited on copper substrate at the current density of 10 mA/cm^2

D. Magnetic Properties

Fig. 4 (a), (b), (c), and (d) show the M-H curve of CoNiWP thin films deposited on copper substrate. From the investigation it is find out that the film exhibits ferromagnetic behavior. The coercivity and squareness of the films were increased when the current density is increased which is given in the table. The increase in current density causes an uniform deposition and higher percentage of magnetic elements, this equally balanced cobalt, nickel, tungsten and phosphorus content in the film prepared at higher current density led to the formation of high coercivity from 1,037 to 3,053 Oe.

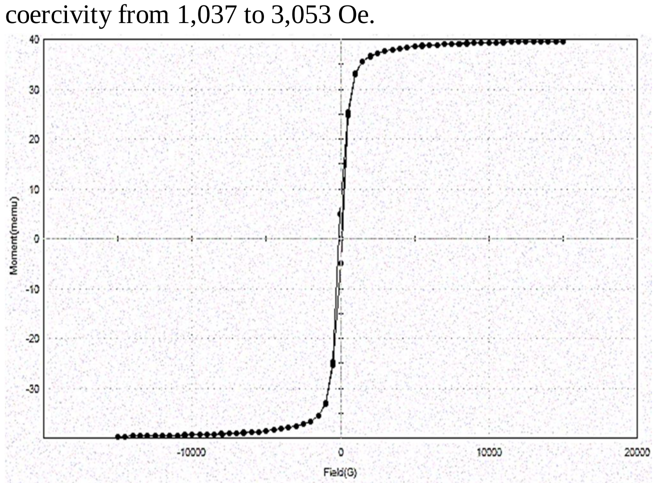

Fig. 4 (a) Hysteresis loop of CoNiWP films deposited on copper substrate at the current density of 2.5mA/cm^2

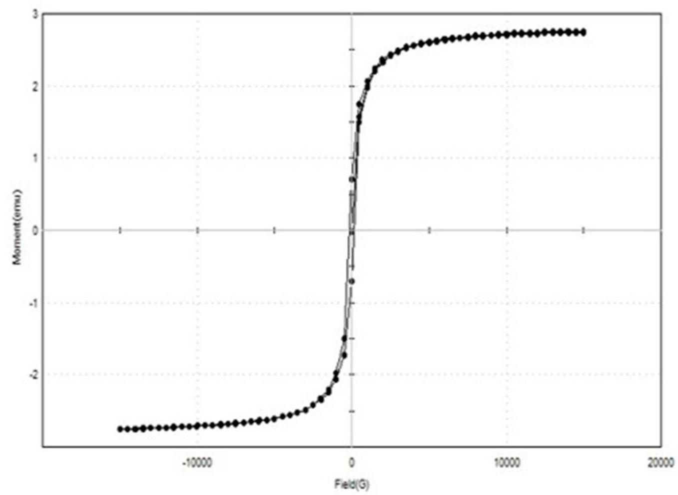

Fig. 4 (b) Hysteresis loop of CoNiWP films deposited on copper substrate at the current density of 5 mA/cm^2

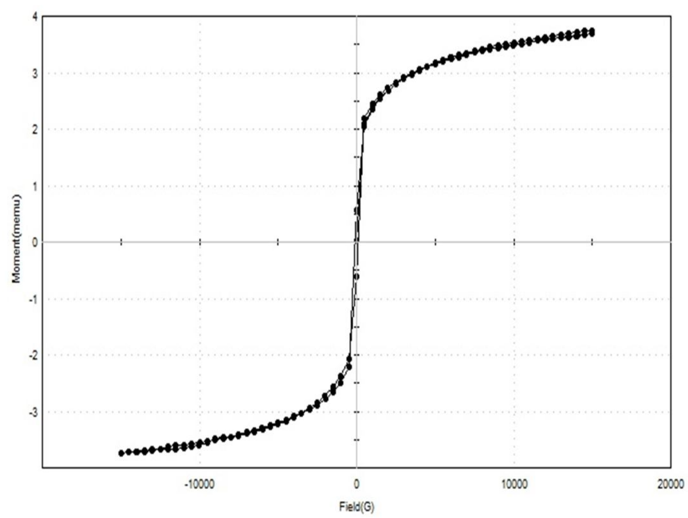

Fig. 4 (c) Hysteresis loop of CoNiWP films deposited on copper substrate at the current density of 7.5 mA/cm^2

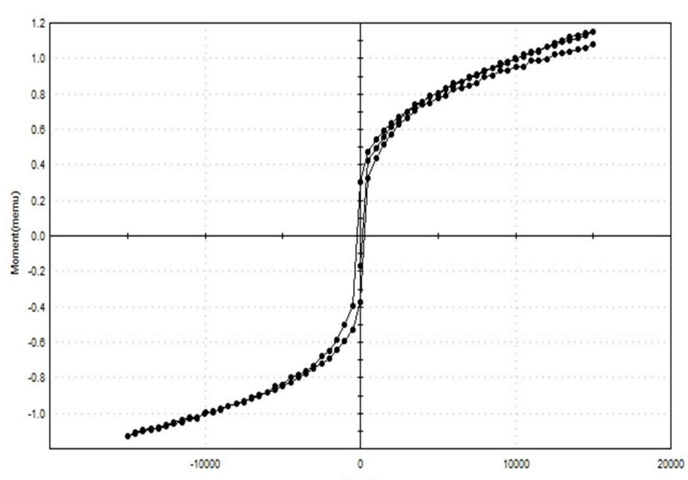

Fig. 4 (d) Hysteresis loop of CoNiWP films deposited on copper substrate at the current density of 10 mA/cm^2

Table Ii Magnetic Properties Of Coniwp Films Deposited At Different Current Density

Bath	substrate	Concentration	Deposition time	Current Density (mA/cm^2)	M_s 10^{-3} emu	M_r 10^{-3} emu	Coercivity O_e	Squareness
Tri Sodium Citrate	copper	0.1	30 minutes	2.5	39.61	4.85	1037	0.12
				5	11.52	1.76	1103	0.15
				7.5	3.73	0.58	1135	0.15
				10	1.14	0.33	3053	0.29

E. Magnetoresistivity Studies

Magnetoresistive behavior of the CoNiWP films were investigated using Four probe technique. Film deposited at the current density of 2.5 and 10 mA/cm^2 which exhibits low and high coercivity has been chosen to study the magneto resistivity behavior. GMR ratio has been calculated by using the magnetoresistivity equation $(R_H-R_0).100/R_0$.[13] This calculated GMR ratio with respect to the magnetic field was plotted and shown in fig.5 (a) and (b). From the obtained result it is noted that GMR ratio was found to be steadily decreases from 30%-17% and 35% to 17% with respect to the applied magnetic field. It is initiated by the applied high current density in the film deposition process. The applied current density in deposition process enhances the constituents in the film which results in improved GMR ratio.

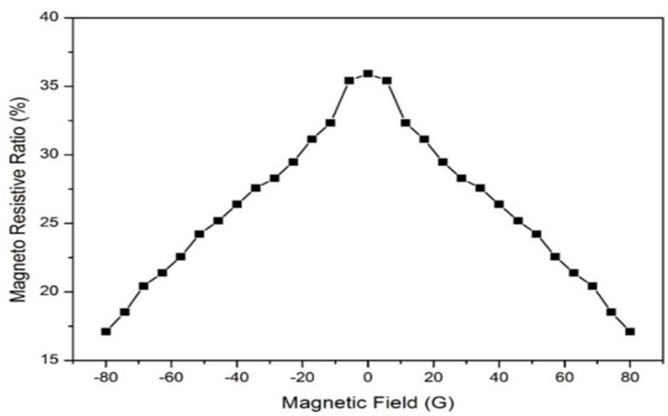

Fig.5(a) Magnetoresistivity response of CoNiWP films deposited at the current density of 2.5 mA/cm^2

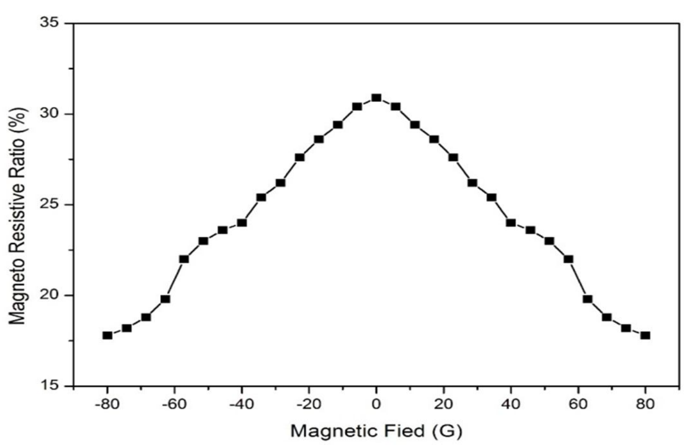

Fig.5(b) Magnetoresistivity response of CoNiWP films deposited at the current density of 10 mA/cm^2

F. Corrosion Studies

Corrosion behavior of a metal and alloys plays a vital role in their mechanical stability; it is mostly affected by their atmosphere. Generally Cobalt and nickel exhibits better corrosion resistance, but on film surfaces their Corrosion resistance have still been observed in real applications under certain unfavorable environments such as acidic environments. Weight loss method was identified as an ideal and simple technique for study the corrosive behavior of a film or metals over other immersion techniques. In present work, weight loss method was employed to evaluate the corrosion rate of the prepared films in an acidic medium. The weight of the samples was measured before immersion and then measured after two days using this total weight loss in the film during the immersion period was calculated. The corrosion rate of the film is assessed by its density, weight loss and exposed area of the film. Using the below equation corrosion rate was calculated. [20-26]

$$Rcorr = \frac{\Delta W}{\rho A t}$$

Where, R_{corr} is Corrosion rate, ΔW is weight loss, ρ is Density, A is immersed area, t is exposed time. The calculated corrosion rate of the films with the exposure time of two days is shown in Fig 6. The corrosion kinetics of the films in acid medium is observed for both copper plate and prepared films. From this investigation it is find out that the corrosion rate is steadily decreased when it is compared with copper plate. Over these, films deposited at 10 mA/cm^2 exhibits better corrosion resistance (269 mpy). This reduction in corrosion rate on the film prepared at 10 mA/cm^2 is due to the formation of a unreceptive film on the surface of CoNiWP film which acts as protective layer that decelerated the corrosion rate.

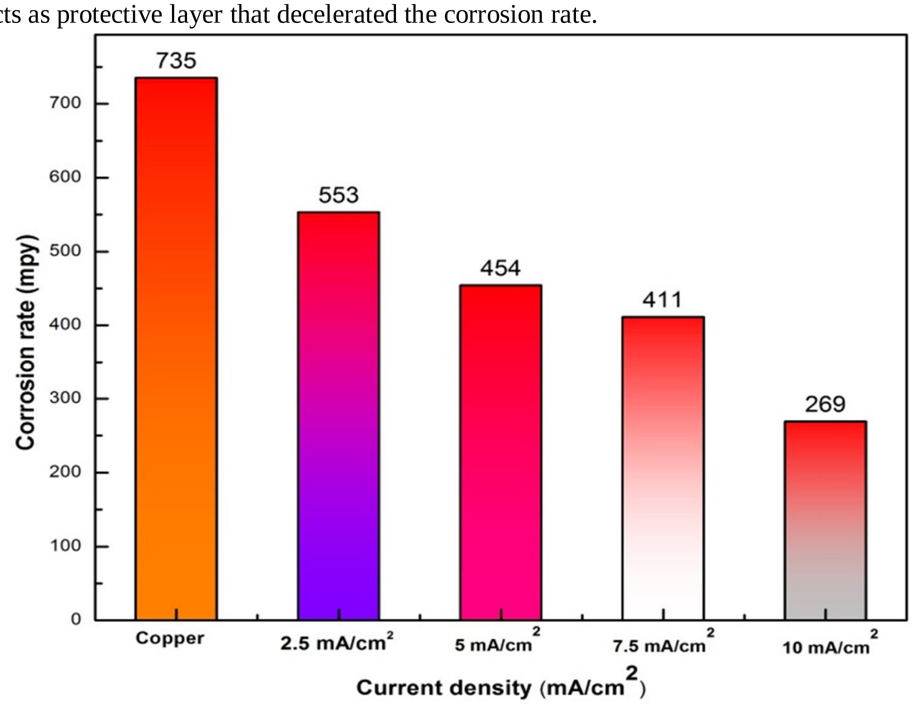

Fig.6 corrosion properties of CoNiWP films deposited at different current density

IV. CONCLUSIONS

CoNiWP alloy was electrodeposited from Citrate based Sulphate bath on Copper substrates by optimizating the deposition parameters. The films were deposited under different current densities. The structural properties of the film reveals the crystallinity and crystallites are in nanoscale for all the films. The morphology of the films were similar for every conditions. The EDAX pattern reveals that the current density shows strong impact on deposition which results in the presence of higher magnetic constituents, and the presence of low level impurity for the film prepared at high current density .The films deposited at the current density of 10 mA/cm^2 shows higher coercivity (3,053 Oe) with better magnetoresistive behavior (17% - 30%). Corrosion studies also reveals that the film deposited at higher current density exhibits good corrosion resistance due to the formation of cobalt and nickel rich films. From this investigation it is concluded that curent density produce significant imrprovement in phosphorous deposition which strongly influences the magnetic behavior. Hence the film deposited at 10 mA/cm^2 seizes more attention than the films deposited with low current densitiy and it is found to be an ideal candidate for GMR based applications.

REFERENCES

[1] T. Baskar, K.S. Rajni, R. Kannan Int. J. Adv. Technol. Eng. Sci 2(10), 293–299 (2014)
[2] K. Mohan, R. Kadiresan, V. Senthilkumar, Int. J. Adv. Res. Sci. Eng. 5(7), 285–292 (2016)
[3] P. Mazalski, I. Sveklo, M. Tekielak, A. Kolendo, A. Maziewski, P. Kuświk, B. Szymański, F.Stobiecki, Materials Science-Poland, 25 (4), 1290-1294 (2007).
[4] Mitra Djamal and Ramli, Advanced Materials Research 770 1-9, (2013)
[5] Y. Li, Ruili Fan, M. Moldovan, D. P. Young, W.Wang and E. J. Podlaha, ECS Transactions, 2 (6) 379-385 (2007)
[6] Inga Ennen, Daniel Kappe, Thomas Rempel, Claudia Glenske and Andreas Hütten, Sensors , 16, 904, 1-24 (2016)
[7] Abdul Halim shaari. Elias Salon. Chow Sal Pew. Hishamuaain Zalnuaaln Appl. Sci and Tech, 2, 379-382 (2000)
[8] N. Rajasekaran and S. Mohan, Critical Reviews in Solid State and Materials Sciences, 37, 158–180, (2012)
[9] Y. Li, M. Moldovan, D. P. Young and E. J. Podlaha, 208th Meeting of The Electrochemical Society, Los Angeles, (2005)
[10] L. Peter, A. Cziraki, L. Pogany, Z. Kupay, I. Bakonyi, M. Uhlemann, M. Herrich,B Arnold, T Bauer, K Wetzig, J. Electrochem. Soc., 148, C168 (2001)
[11] N. Tsynlsaru, J. Bobanova, X. Ye, H. Cesiulis, A. Dikusar, J.-P. Prosycevas, Surf. Coat. Technol. 203(20–21), 2983–3332 (2009)
[12] A. Bodaghi, J. Hosseini, Int. J. Electrochem. Sci. 7, 2584–2595 (2012)
[13] R.N. Emerson , C. Joseph Kennady, S. Ganesan, Thin Solid Films 515, 3391–3396 (2007)
[14] Ezhil Inban Manimaran, Emerson Rajamony Navaneetha, J Mater Sci: Mater Electron, (2015)
[15] R. Raj Kumar P. Gowrisankar V. Balaprakash ·S. Sudha, Ezhil Inban Manimaran J. Mater. Sci
[16] B.Y. Yoo a, S.C. Hernandez a, D.-Y. Park b, N.V. Myung a, Electrochimica Acta 51 (2006) 6346–6352
[17] E.I. Manimaran, K. Antonyraj, E.R. Navaneetha, J. Mater. Sci 29(5), 3715–3721 (2018)
[18] M.R. Kadiresan, V. Senthil Kumar, Int. J. Adv. Res. Sci. Eng. 5(7),285 (2016)
[19] K.M. Hyie, W. Normini, R. Abdullah, N. A. Resali, W.T. Chong, Z. Salleh, M.A.A. Ghanni, J. Nanomater., 680491 (2013)
[20] A. Y. El-Etre Corr. Sci. 45 2485 (2003).
[21] S.A. Umoren and E. E. Ebenso, Matls. Chem. Phys., 106, 387 (2007).
[22] M. M. El-Naggar, Corr. Sci. 49, 2226 (2007)
[23] M. Lebrini, F. Bentiss, H. Vezin and M. Lagrenee, Corr. Sci. 48, 1279 (2006).
[24] A. S. Afolabi , A. C. Muhirwa, A. S Abdulkareem and E. Muzenda Int. J. Electrochem. Sci., 9, 5895 – 5906 (2014).
[25] F.V. Adams, P.A. Olubambi, J.H. Potgieter, J. Van Der Merwe. J. Anti-Corr Metds & Matls., 57, 107 (2010).
[26] S. S. Abd El Rehim, S. M. Sayyah, M. M. El-Deed, S. M. Kamal, and R. E. Azooz, Matls. Chem. Phys., 123, 20 (2010).